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(71)Applicant : MATSUSHITA ELECTRIC IND CO LTD

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(72)Inventor : NAGATA HIROMI

KITAGAWA MASAKI

MURAI SUKEYUKI

TAKEUCHI TAKASHI

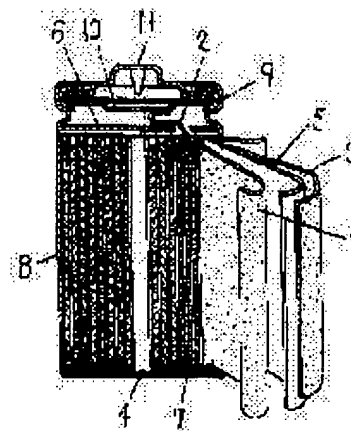
MORITA TERUYOSHI

(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide a nonaqueous electrolyte secondary battery which is excellent in a large current discharging characteristic by putting a scale-shaped graphite having a property excellent as a negative electrode material in an electrode condition suitable for large current discharging in capacity to store and release lithium and filling performance of carbon powder.

CONSTITUTION: Spherical graphite is contained in a negative electrode active material layer contacting a collector material, and scale-shaped graphite is contained in an active material layer on the surface of a negative electrode, and a rate of the spherical graphite is set to 20% to 80% in the weight ratio. Fibered graphite is also added 5% to 20% to at least either one of the active material layers.



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CLAIMS

[Claim(s)]

[Claim 1] It is the nonaqueous electrolyte rechargeable battery characterized by consisting of a metal thin film which are the active material layer which consists of mixture of the graphite and binder whose aforementioned negative electrode is negative-electrode material in the nonaqueous electrolyte rechargeable battery which rolls a positive electrode and a negative electrode in the shape of a swirl, carries out a time, and constitutes them through separator, and current collection material, containing a nodular graphite in the active material layer which touches current collection material, and containing a scale-like graphite in the active material layer on the front face of a negative electrode.

[Claim 2] The nonaqueous electrolyte rechargeable battery of the nodular graphite which is negative-electrode material, and a scale-like graphite according to claim 1 which added the fibrous graphite to either at least.

[Claim 3] The nonaqueous electrolyte rechargeable battery according to claim 1 or 2 whose rate of the nodular graphite occupied to the graphite which is negative-electrode material is 20% or more 80% or less of range by the weight ratio.

[Claim 4] The nonaqueous electrolyte rechargeable battery according to claim 2 or 3 whose rate of the fibrous graphite occupied to the graphite which is negative-electrode material is 5% or more 20% or less of range by the weight ratio.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to an improvement of a nonaqueous electrolyte rechargeable battery, especially a negative electrode.

[0002]

[Description of the Prior Art] The requests of small and lightweight-izing are mounting also to the cell as the power supply as the miniaturization of electronic equipment and lightweight-ization progress. As for the nonaqueous electrolyte rechargeable battery which uses a lithium metal for a negative electrode especially, it has had a hope from a large bird clapper with the great theoretical energy density. However, when a lithium metal is used for a negative electrode, while the lithium (dendrite) of arborescence generates at the time of charge and the charge and discharge of a cell are repeated, this dendrite grows, separator is penetrated, there are problems, such as causing the internal short circuit of a cell and leading to ignition of a cell further, in [that] being extreme, and completeness is not solved until it continues till present.

[0003] Although the attempt which is not lithium metal independent and uses the alloy of low melting point metals, such as aluminum, lead, an indium, a bismuth, and cadmium, and a lithium as a negative electrode as a means to solve this problem has been made variously It is hard to say that it was solved since an alloy turned minutely, this detailed alloy penetrated separator and the short circuit of a cell and ignition occurred like a lithium metal negative electrode while repeating the occlusion of the lithium into an alloy, and discharge in connection with the charge and discharge of a cell also in this case.

[0004] On the other hand, the cell which uses carbon for a negative electrode was proposed as what solves the above-mentioned problem. The cell using carbon as a negative electrode of a nonaqueous electrolyte rechargeable battery is introduced to the collection P.97 of the 1986 27th cell debate summaries per year, or the collection P.201 of the 1987 28th cell debate summaries per year, and is supposed that the lithium which is an active material is twisted to the electrochemical technique in the outside of a fuel cell subsystem as a method of making it support into the carbon of a negative electrode, using a vanadium pentoxide, manganese dioxide, or a chrome oxide as a positive active material. It is put in practical use as a coin form cell by which the cell which used the vanadium pentoxide for the positive electrode and used carbon for the negative electrode is mainly used for a memory backup use etc. especially, and the method of contacting a lithium metal and carbon electrically is taken within the cell as the support method of the lithium to a negative electrode.

[0005] It continues till recently, the cylindrical shape cell which used LiCoO_2 for the positive electrode and used carbon for the negative electrode by the collection P.83 of the 1992 33rd cell debate summaries per year is proposed as a power supply for electronic equipment, and after 1200 cycle progress is reported to have held 70% or more of early capacity in the charge and discharge of deep depth. Now, this fuel cell subsystem is put in practical use as a 4 Class V rechargeable lithium-ion battery in each company. The features of this fuel cell subsystem are the occlusion of the lithium ion to the inside of the carbon of a negative electrode, and release reaction, and since a deposit of the lithium to the negative-electrode top accompanying charge does not start, therefore a dendrite does not arise, the charge-and-discharge reaction of a negative electrode has them in the place referred to as that a good cycle property is acquired. Simultaneously, another feature of this fuel cell subsystem uses for the positive electrode a lithium content oxide called LiCoO_2 , and since the lithium which is a negative-electrode active material is supplied from a positive electrode, it is in the place which says that it is not necessary to make a negative electrode support a lithium by the special place method.

[0006] What replaced not only above LiCoO_2 but LiNiO_2 , LiMn_2O_4 , LiFeO_2 , or these [Co, nickel, Mn, and Fe] in part by other metallic elements as a positive active material of 4 Class V rechargeable lithium-ion battery is examined until now. Moreover, as carbon which is negative-electrode material, although it has inquired at the beginning centering

on the so-called amorphous carbon, such as a low-temperature burned product of corks, a pyrolytic carbon, or the various organic substance, recently, the carbon of high crystallinity and the carbon of the so-called graphite system attract attention from a viewpoint of the occlusion of the lithium which is an active material, and discharge capacity. [0007] It is supposed that the property the graphite material which consists of the spherical particle of graphitizability as a negative electrode excelled [property] in JP,4-115457,A is shown. C₆Li which is the intercalation compound of a graphite and a lithium is known for many years, and electrochemically, occlusion and when it emits (an intercalation, day intercalation), geometric capacity shows the very big value of 372mAh(s) for a lithium to carbon 1g. Nevertheless, when the propylene carbonate widely used as one of the solvent components of the electrolytic solution with the present nonaqueous electrolyte primary cell was used as reported by Journal of Electrochemical Society 117 and No.2 (1970) p.222, not having been adopted as a negative electrode of a rechargeable lithium-ion battery at the beginning decomposed on the surface of the graphite, and its solvent molecule of the suited to an intercalation reaction into the graphite of a lithium not being performed smoothly. On the other hand, it is reported by using ethylene carbonate for the solvent component of the electrolytic solution as a subject by the collection P.238 of the 1992 59th electrochemistry convention lecture summaries per year that this problem is solved. Henceforth, a natural graphite and various artificial graphites are examined as a negative electrode of a rechargeable lithium-ion battery, and are becoming in use [the negative electrode of a graphite system] rather now.

[0008] On the other hand, the restoration nature how a lot of carbon can be stuffed is in limited volume called a cell with the occlusion of the own lithium of carbon, and the capacity of discharge as requirements searched for as a negative electrode of a cell, and if this is not only carbon but powder, it will be greatly influenced by the configuration.

[0009] It is divided roughly into the shape of a grain, mass, and a scale, and fibrous four when the configuration of carbon powder is considered. Although carbon and the mixed paste of a binder are usually applied to both sides or one side of a metal thin film which is a charge collector, it rolls out suitably after drying what was made into the plate and an electrode is formed in a lithium ion battery, among the four above-mentioned sorts of configurations, scale-like carbon is most excellent in restoration nature. That is, although the configuration of a particle does not change even if it rolls out with the carbon of other three sorts of configurations, after drying a plate, but it only fills up only densely, in order that a particle may carry out orientation of the scale-like carbon in the same direction with rolling, large next door restoration nature also serves as [close nature] size more. Therefore, in the viewpoint of the occlusion of a lithium, the capacity of discharge, and the restoration nature of carbon powder, it can be said that it is the material it is nature or an artificial graphite, and the powder configuration excelled [material] in the scale-like thing most as a carbon negative-electrode material.

[0010] However, if it takes into consideration that the material by the special processing for removing the variation of the material by the difference in the production ground or a lot of impurities etc. needs to be managed in the case of a natural graphite, it can be said that a scale-like artificial graphite is most excellent as a carbon negative-electrode material. It is what graphitized the coal pitch or the petroleum pitch as an artificial graphite of the shape of a typical scale, and the artificial graphite by the Lonza make or the Japanese graphite company is raised.

[0011]

[Problem(s) to be Solved by the Invention] However, when using a scale-like artificial graphite as a negative-electrode material, one technical problem which must be solved occurs. sure -- a scale-like graphite -- a stacking tendency -- eye a big hatchet -- rolling -- although restoration nature goes up, restoration nature goes up too much conversely, the hole portion in an electrode is restricted, since the electrolytic solution does not permeate the interior of an electrode when the electrode of a cell is formed, a cell reaction is performed only in the surface portion of an electrode, but the technical problem are not suitable for the decline in a reaction utilization factor or strong electric discharge of an electrode arises

[0012] this invention solves the above-mentioned technical problem, and it aims at offering the nonaqueous electrolyte rechargeable battery made into the plate state suitable for strong electric discharge using the graphite which has the property which was excellent as a negative-electrode material.

[0013]

[Means for Solving the Problem] In order to solve these technical problems, this invention adds a fibrous graphite to either, even if there are few these active material layers, when a nodular graphite shall be contained in the negative-electrode active material layer which touches current collection material, a scale-like graphite shall be contained in the active material layer on the front face of a negative electrode and you need especially a cycle property.

[0014]

[Function] Usually, although it prepared like the roll turner at the time of negative-electrode board production and the active material was changed into the suitable restoration state, when a scale-like graphite is used for an active material, since a scale-like graphite is the property to be easy to roll out, it is difficult for it to control to the pack density holding the suitable hole volume for liquid fully permeating to the optimal pack density, i.e., the interior of a plate, and all

active materials reacting. Moreover, since it is in the state to which it was hard to carry out in-and-out of a lithium ion at the time of charge and discharge, and the scale lapped on the metal thin film which is a charge collector since the hex-steel side of a graphite will be in the state where orientation was carried out in parallel with an electrode front face, with rolling, even if it rolls out, a scale and a metal thin film are slippery, a graphite particle does not eat into a charge collector, but the contact intensity of a charge collector and a graphite particle is comparatively weak.

[0015] On the other hand, although it is comparatively hard to fill up with a nodular graphite, since it is the structure (lamella structure) where the edge of the hex-steel side of a graphite exists in a particle front face, receipts and payments of the lithium ion accompanying charge and discharge are performed comparatively smoothly. Moreover, it is easy to eat also into the metal thin film which is a charge collector, and excels comparatively also in respect of the contact intensity of a charge collector and a graphite particle.

[0016] The nonaqueous electrolyte rechargeable battery excellent in the strong electric discharge property can be constituted by using the negative-electrode board made into the structure which arranges a nodular graphite to the active material layer which touches a charge collector from the above thing, secures contact intensity with a charge collector, arranges a scale-like graphite to the active material layer on the front face of an electrode, and increases the fill of an active material.

[0017] Furthermore, it covers by arranging on the electrode front face in which it covers according to the structure of the nodular graphite which a lithium ion tends to frequent in the point that movement of a lithium is difficult in distance since the active material layer to which this structure touches a charge collector is distant from the electrode front face, and a reaction occurs most smoothly the point of a scale-like graphite that movement of a lithium is difficult in particle shape.

[0018] Moreover, although a good cell property is not acquired even if a fibrous graphite has still lower restoration nature and it uses it independently rather than a spherical particle geometrically, in order to secure the hole of a proper quantity to the shape of a scale, and a spherical particle by carrying out little addition and to increase liquid wettability and a reaction surface area, an effect is in improvement of a strong electric discharge property. Furthermore, by securing the hole of a proper quantity, the volume change by expansion of the carbon particle accompanying charge and discharge and contraction can be absorbed, decay of a plate can be suppressed, and a cycle property can be improved.

[0019]

[Example] Hereafter, the example of this invention is explained with a drawing. It evaluated by constituting the cell of a cylindrical shape in an example.

[0020] (Example 1) Drawing of longitudinal section of the cylindrical shape cell used for drawing 1 at this example is shown. After plastering both sides of an aluminum foil with what was mixed the water dispersion of polytetrafluoroethylene by the weight ratio as electric conduction material, and was mixed at a rate of 100:3:10 as binding material, drying to LiCoO₂ which 1 shows a positive electrode in drawing and is an active material and rolling out carbon black to it, it cuts in a predetermined size. Spot welding of the positive-electrode lead board made from the titanium of 2 is carried out to this. In addition, the mixed ratio of the water dispersion of the polytetrafluoroethylene of a binder is calculated by the solid content. It is a negative electrode, 3 makes carbonaceous material the main material, and after it plasters both sides of a nickel foil with what was mixed at a rate of 100:5 by the weight ratio, dries and rolls out this and an acrylic binder, it cuts it in a predetermined size. Spot welding of the negative-electrode lead board made from the nickel of 4 is carried out to this. It is the separator which consists of a microporosity film made from polypropylene, and 5 intervenes between a positive electrode 1 and a negative electrode 3, and the whole is wound spirally and it constitutes the group of electrode. It inserts in the case 8 which arranged the up electric insulating plate 6 made from polypropylene, and the lower electric insulating plate 7 on the edge of the upper and lower sides of this group of electrode, respectively, and carried out nickel plating to iron. And after using the positive-electrode lead board 2 as the obturation board 10 made from titanium and using spot welding of the negative-electrode lead board 4 to the bottom of a case 8, respectively, the electrolytic solution of the specified quantity is poured in into a case, a cell is obturated with the obturation board 10 through a gasket 9, and it considers as a completion cell. The size of this cell is 50mm in the diameter of 14mm, and height. In addition, 11 is the positive-electrode terminal of a cell and, as for the negative-electrode terminal, the cell case 8 serves as this.

[0021] The electrolytic solution used what dissolved the 6 fluoride [phosphoric-acid] lithium in the solvent which mixed ethylene carbonate and diethyl carbonate by the mole ratio 1:1 by the concentration of one mol/l. as a solute.

[0022] Five kinds of negative electrodes which elect the Lonza artificial graphite and the mesophase microsphere calcinated at 3000 degrees C as negative-electrode material as a scale-like graphite and a nodular graphite, respectively, and are shown using them (Table 1) were produced, and it included in the above-mentioned cylindrical shape cell, and considered as cell A-E. What makes the graphite layer of a negative electrode a bilayer applied the eye on current collection material further first, and applied the bilayer eye on it.

[0023] When any negative electrode was rolled out on the same conditions at that time and it produced so that it might become the same thickness, since restoration nature was good compared with a nodular graphite, in the scale-like graphite, the active material weight per plate became large.

[0024] Moreover, since the purpose of this example was seeing the difference of the property by the negative electrode, to the amount of negative-electrode active materials, the amount of positive active materials was fully large, and it considered as the composition which outputs the capacity of about 600 mAhs on the experiment conditions shown below.

[0025] Constant-current discharge of five kinds of cells shown above was carried out with a low current and high current, and service capacity was measured. After it made the test condition into 100mA of charge and discharge currents, charge final-voltage 4.2V, discharge-final-voltage 3.0V, and the environmental temperature of 20 degrees C and it repeated charge and discharge 5 times, it changed only the discharge current into 500mA, and performed charge and discharge. The high current service capacity to the service capacity of 5 cycle eye in a low current, the service capacity in high current, and low-current service capacity reaches comparatively, and the graphite weight per negative-electrode board of each cell is shown in (Table 1).

[0026]

[Table 1]

| 電池 | 負極黒鉛混合比率（重量比／％） | | | 低電流 | 高電流 | 高電流／低電流 | 負極1枚当たりの |
|----|-----------------|-----|-------------|---------------|---------------|-------------|-------------|
| | 鱗片状 | 球状 | 鱗片状／球状の存在状態 | 放電容量 (mAh) | 放電容量 (mAh) | 容量比率 (％) | 黒鉛重量 (g) |
| A | 50 | 50 | 二層(表面／集電材側) | 524 | 472 | 90 | 2.14 |
| B | 50 | 50 | 二層(集電材側／表面) | 505 | 367 | 78 | 2.14 |
| C | 50 | 50 | 単一層(混在) | 511 | 419 | 82 | 2.07 |
| D | 100 | 0 | 単一層 | 475 | 238 | 50 | 2.40 |
| E | 0 | 100 | 単一層 | 483 | 459 | 95 | 1.93 |

[0027] Since the cell of this example is composition with a sufficient positive-electrode capacity, any cell of the potential change accompanying the charge and discharge of a positive electrode is small similarly, and the lithium occlusion capacity of a negative electrode reaches a limitation in the charge last stage, negative-electrode potential falls rapidly, and charge capacity is determined by the phenomenon in which charge is completed when the potential difference of positive and a negative electrode serves as charge final voltage. On the other hand, any cell of the charge-and-discharge efficiency at the time of discharging by the low current is about 100%, the charge-and-discharge efficiency at the time of service capacity being determined by charge capacity and discharging with high current becomes 100% or less, and service capacity is determined by the ease of the reaction at which a lithium moves in the inside of a negative electrode at the time of electric discharge.

[0028] From (Table 1), when comparison by the kind of graphite was performed, the service capacity in a low current became smaller than the cell [way / of the cell D which used the scale-like graphite] E using the nodular graphite. It is thought that there was also little charge capacity since, as for Cell D, the electrolytic solution does not fully permeate in fact since the pack density of a graphite is high and the hole volume inside a plate is small although in original and Cell D service capacity should become large compared with Cell E since the graphite weight is large, and a reaction does not fully occur, and service capacity also became small as a result.

[0029] On the other hand, as for the service capacity in high current, the difference became large further. these things to a scale-like graphite -- low and quantity current -- any electric discharge had a small capacity and was found by that especially a strong electric discharge property is inferior

[0030] Although the service capacity in a low current became the order of cell A-C-B about the mixed stock of cell A-C as compared with the next, and the not much remarkable difference was not seen, capacity was size from the scale-like graphite independent cell D and the nodular-graphite independent cell E.

[0031] On the other hand, although the service capacity in high current was also the order of cell A-C-B, especially the difference was remarkable. The scale-like graphite with which the reaction of a lithium cannot occur easily since there are few holes and the electrolytic solution cannot permeate easily by Cell A this When it exists in the negative-electrode front face on which a reaction occurs smoothly and the nodular graphite which has secured the proper

quantity hole exists in a current collection material front face Since a scale-like graphite exists in the place which touches the remote current collection material of distance from a negative-electrode surface layer by Cell B to being for the move reaction of the lithium accompanying charge and discharge to advance comparatively smoothly, it guesses because the move reaction of a lithium is not performed not much smoothly. Since a scale-like graphite is distributed over the whole plate, Cell C is imagined to be the middle reaction state of Cells A and B.

[0032] It was the cell A of this invention that was [a low current and any current value of high current] large as comprehensive evaluation as for service capacity the above result.

[0033] (Example 2) a nodular graphite is the optimal with the composition of the negative-electrode board of the cell A in which the best property was shown in the example 1 -- a mixing ratio -- it evaluated by making the aforementioned cylindrical shape cell as an experiment about six kinds of negative electrodes shown in order to ask for a rate (Table 2) Evaluation measured the constant-current discharge capacity in a low current and high current like the example 1.

[0034] The result of evaluation is shown in (Table 2).

[0035]

[Table 2]

| 電池 | 負極黒鉛混合比率（重量比／％） | | | 低電流 | 高電流 | 高電流/低電流 | 黒鉛1g当たりの |
|----|-----------------|----|-------------|---------------|---------------|-------------|-------------|
| | 鱗片状 | 球状 | 鱗片状／球状の存在状態 | 放電容量 (mAh) | 放電容量 (mAh) | 容量比率 (％) | 黒鉛重量 (g) |
| F | 90 | 10 | 二層(表面／集電材側) | 478 | 263 | 55 | 2.39 |
| G | 80 | 20 | 二層(表面／集電材側) | 536 | 440 | 82 | 2.33 |
| H | 60 | 40 | 二層(表面／集電材側) | 539 | 474 | 88 | 2.22 |
| I | 40 | 60 | 二層(表面／集電材側) | 517 | 470 | 91 | 2.10 |
| J | 20 | 80 | 二層(表面／集電材側) | 503 | 467 | 93 | 2.03 |
| K | 10 | 90 | 二層(表面／集電材側) | 486 | 457 | 94 | 1.95 |

[0036] It turns out that it is so small that the active material layer weight per negative-electrode board serves as cell F-G-H-I-J-K at descending and the mixed ratio of a nodular graphite increases more than (Table 2).

[0037] In the cell property, the service capacity in a low current became cell H-G-I-J-K-F at descending, and capacity was low at the minimum and composition of the maximum [ratio / mixed / of the nodular graphite of Cell F and Cell K]. Like the cell A of an example 1, the ratio of a scale-like graphite is large, pack density goes up the reason nil why the capacity of Cell F is small, too much, it thinks because the reaction inside a plate was inadequate, and on the other hand, the ratio of a nodular graphite is large and the reason nil why the capacity of Cell K is small is considered to be Cell F because pack density is low on the contrary.

[0038] Moreover, the service capacity in high current became cell H-I-J-K-G-F at descending, and especially its cell F was small. The rate of the service capacity in the high current over the service capacity in a low current became so large that the mixed ratio of a nodular graphite is high. With the inclination for this to also have been seen also in the example 1, on the surface of a particle, since the occlusion of a lithium and the entrance of discharge exist mostly, the way of a nodular graphite is considered because it is advantageous to electric discharge with high current.

[0039] as comprehensive evaluation -- a low current and high current -- the service capacity in which current value maintains balance in total -- cell G-J -- it is -- the mixing ratio of a nodular graphite -- the rate was 20 - 80% (weight ratio) of range

[0040] (Example 3) in order to investigate the addition effect of a fibrous graphite with the composition of the negative-electrode board of the cell E in which the best property was shown in the example 1, it is shown in (Table 3) -- trial production of the above-mentioned cylindrical shape cell and evaluation were performed about six kinds of negative electrodes The evaluation method suspended the examination, when the discharge current value was returned to 100mA, charge and discharge were repeated and service capacity decreased to 50%, after measuring the service capacity in a low current and high current like examples 1 and 2, and it made the number of charge-and-discharge cycles at that time the cycle life of the cell.

[0041] What carried out high temperature processing of the vapor-growth carbon fiber by Showa Denko K.K. was used for the fibrous graphite.

[0042] The result of evaluation is shown in (Table 3).

[0043]

[Table 3]

| 電池 | 負極黒鉛混合比率 (重量比/%) | | | | 低電流 | 高電流 | 高電流/低電流 | サイクル | 黒鉛重量 |
|----|------------------|--------|-------|-------------|---------------|---------------|-------------|--------------|-------------|
| | 黒鉛板/黒鉛板 | 比率/混合比 | 黒鉛板合計 | 黒鉛板/電極材料 | 放電容量 (mAh) | 放電容量 (mAh) | 容量比率 (%) | 寿命 (サイクル) | 黒鉛重量 (g) |
| L | 50/0 | 50/0 | 0 | 二層(黒鉛/電極材料) | 524 | 472 | 90 | 500 | 2.14 |
| M | 50/0 | 45/5 | 5 | 二層(黒鉛/電極材料) | 450 | 414 | 92 | 1000 | 1.80 |
| N | 45/5 | 50/0 | 5 | 二層(黒鉛/電極材料) | 450 | 414 | 92 | 1100 | 1.80 |
| O | 45/5 | 45/5 | 10 | 二層(黒鉛/電極材料) | 420 | 395 | 94 | 1300 | 1.65 |
| P | 40/10 | 40/10 | 20 | 二層(黒鉛/電極材料) | 400 | 380 | 95 | 1400 | 1.54 |
| Q | 35/15 | 35/15 | 30 | 二層(黒鉛/電極材料) | 360 | 346 | 96 | 1500 | 1.36 |

[0044] It is so small [the graphite weight per / to which the fibrous graphite added the fibrous graphite since ** was high compared with a scale-like graphite and a nodular graphite / plate is smaller than (Table 3) compared with the plate which is not added, and] that the mixed ratio of a fibrous graphite becomes large.

[0045] In the cell property, it became so small that the service capacity in a low current serves as cell L-M and N-O-P-Q at descending and the mixed ratio of a fibrous graphite becomes large, and especially the thing of the maximum [ratio / of the fibrous graphite of Q] had a small capacity. By its hole volume in a plate increasing, so that this contains many fibrous graphites, although a next door and the reaction depth of an active material increase enough, since ** of a fibrous graphite is large, by one side, the active material weight per plate becomes small, and osmosis of the electrolytic solution is considered because charge-and-discharge capacity becomes small.

[0046] Although the service capacity in high current became descending with cell L-M and N-O-P-Q similarly, the rate of the service capacity in the high current over the service capacity in a low current was so large that the ratio of a fibrous graphite was high, and the high current electric discharge property found that addition of a fibrous graphite was effective for it. Moreover, whichever it added [of a scale-like graphite and a nodular graphite] the fibrous graphite, there was no difference in service capacity.

[0047] On the other hand, the cycle life became cell Q-P-O-N-M-L at long order, the cycle life was prolonged by leaps and bounds by addition of a fibrous graphite, and the cycle life became long, so that the addition ratio was large. When a fibrous graphite exists in the crevice between the particles of a scale-like graphite or a nodular graphite, this prevents collapse of the plate by expansion of the particle at the time of charge and discharge and contraction, and is guessed because it has the effect of improving contact between particles. Moreover, the cell N of the life added in the scale-like graphite layer was longer than the cell M added in the nodular-graphite layer. Since a scale-like graphite has good restoration nature, it has little hole volume in a plate, and this cannot absorb expansion of the carbon particle accompanying charge and discharge, and contraction, when a scale-like graphite is compared with a nodular graphite. Therefore, if the plate volume change at the time of charge and discharge is large and repeats a charge-and-discharge cycle, the binding capacity between carbon particles will decline gradually, and it will be accompanied by decay of a plate. The addition effect of a fibrous graphite over the property to be easy to fill up with this scale-like graphite, i.e., the effect which suppresses decay of the plate accompanying a cycle, is guessed because it is larger than the addition effect to a nodular graphite.

[0048] If the above is summarized, although some service capacity in a low current and high current will fall by adding a fibrous graphite, a cycle-life property improves by leaps and bounds. Therefore, when a cycle-life property is thought as important, the system which added the fibrous graphite is suitable, and the mixed ratio in that case has 5 - 20% (weight ratio) of the whole good range. moreover, the effect -- a scale-like graphite layer and a nodular-graphite layer -- although it was obtained even when it added in which layer, the improvement effect was size when it added in a scale-like graphite layer especially

[0049] allotting a nodular-graphite layer to the field in contact with the current collection material of a negative electrode by 20 - 80% of the whole weight ratio, and allotting a scale-like graphite layer on the surface of a negative electrode putting the result of the above three examples together, -- a low current and high current -- any electric discharge property can improve Although some service capacity fell by adding 5 - 20% of fibrous graphite to the

- weight of the whole negative-electrode graphite in one of graphite layers further at least, it turns out that a cycle-life property can be improved by leaps and bounds.

[0050] Therefore, to the use which thinks service capacity, i.e., an energy density, as important, the composition which does not add a fibrous graphite among the above-mentioned negative-electrode composition is suitable, and the composition which added the fibrous graphite to the use which thinks a cycle-life property as important on the other hand is suitable.

[0051] In addition, although the multiple oxide of a lithium and cobalt was used for the positive active material in this example, even when the thing of lithium content oxides, such as a multiple oxide of other positive active materials, for example, a lithium, the multiple oxide of nickel and a lithium, the multiple oxide of manganese and a lithium, and iron, or the above-mentioned multiple oxide which replaced cobalt, nickel, manganese, and iron in part by other transition metals, respectively was used, the almost same effect was acquired.

[0052] Moreover, although the 6 fluoride [phosphoric-acid] lithium was used for the solute of the electrolytic solution in this example, even when other lithium content salts, for example, lithium fluoride, a lithium perchlorate, a trifluoromethane sulfonic-acid lithium, a 6 fluoride [arsenic acid] lithium, etc. were used, the almost same result was obtained.

[0053]

[Effect of the Invention] By allotting a nodular-graphite layer to the field which contacts the current collection material of a negative electrode by the above explanation according to this invention so that clearly by 20 - 80% of the whole weight ratio, and allotting a scale-like graphite layer on the surface of a negative electrode Excel in a service-capacity property by any discharge current, and one of graphite layers is received further at least at the weight of the whole negative-electrode graphite. a low current and high current -- The nonaqueous electrolyte rechargeable battery excellent in electric discharge with high current and the cycle-life property can be offered by adding 5 - 20% of fibrous graphite.

[Translation done.]